



Supporting Information

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## **Fast Ion Transfer Processes at Nanoscopic Liquid/Liquid Interfaces**

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# 1. Two models for calculating the steady-state current for an ion egress reaction at nano-ITIES supported at nanopipettes

## 1.1 Schwarz-Christoffel conformal mapping.

The first model is Schwarz-Christoffel conformal mapping.<sup>[1]</sup> It is assumed that the pipette is a hyperbola the shape of which is given by an angle  $v_p$ , such that the equiconcentration lines are ellipses (Figure S1). We consider the following change of variables

$$x = \cosh u \cos v = r \cos v_p / r_{\text{tip}} \quad (\text{s1})$$

$$y = \sinh u \sin v = Y \cos v_p / r_{\text{tip}} \quad (\text{s2})$$

$u$  is the dimensionless concentration defined by  $u = c / c^b$ ,

$v$  is the dimensionless distance along the ellipse

$$\text{Hyperbola: } \frac{x^2}{\cos^2 v} - \frac{y^2}{\sin^2 v} = 1 \quad (\text{s3})$$

$$\text{Ellipse: } \frac{x^2}{\cosh^2 u} + \frac{y^2}{\sinh^2 u} = 1 \quad (\text{s4})$$

The angle  $v$  is defined such that  $\tan(v)$  represents the tapering of the pipette. We have the following correspondences

$$x = 0, y = 0, u = 0, v = \pi / 2 \quad (\text{s5})$$

$$x = \cos v_p, y = 0, u = 0, v = v_p \quad (\text{s6})$$

At the interface, we have  $c(r < r_{\text{tip}}, y = 0) = 0$ , which here is written  $u=0$  for  $v_p < v < \pi/2$ .

By taking the following partial derivatives, we get

$$\frac{\partial x}{\partial x} = 1 = \sinh u \cos v \left( \frac{\partial u}{\partial x} \right) - \cosh u \sin v \left( \frac{\partial v}{\partial x} \right) \quad (\text{s7})$$

$$\frac{\partial y}{\partial y} = 1 = \cosh u \sin v \left( \frac{\partial u}{\partial y} \right) + \sinh u \cos v \left( \frac{\partial v}{\partial y} \right) \quad (\text{s8})$$

From which we get

$$v = 0, \left( \frac{\partial u}{\partial x} \right) = \left( \frac{\partial v}{\partial y} \right) \quad (\text{s9})$$

$$u = 0, \left( \frac{\partial u}{\partial y} \right) = - \left( \frac{\partial v}{\partial x} \right) \quad (\text{s10})$$

The current is defined as

$$I = -nFD \int_0^{r_{\text{tip}}} 2\pi r \left( \frac{\partial c}{\partial y} \right)_{y=0} dr = -\frac{nFD r_{\text{tip}}}{\cos v_p} \int_0^{\cos v_p} 2\pi x \left( \frac{\partial c}{\partial y} \right)_{y=0} dx \quad (\text{s11})$$

We can introduce the dimensionless concentration

$$\left( \frac{\partial c}{\partial y} \right)_{y=0} = c^b \left( \frac{\partial u}{\partial y} \right)_{y=0} \quad (\text{s12})$$

And get

$$I = -\frac{nFD r_{\text{tip}}}{\cos v_p} \int_0^{\cos v_p} 2\pi x c^b \left( \frac{\partial u}{\partial y} \right)_{y=0} dr \quad (\text{s13})$$

We can calculate the integral using the second identity

$$\begin{aligned}
I &= \frac{nFD r_{\text{tip}}}{\cos v_p} \int_0^{\cos v_p} 2\pi x c^b \left( \frac{\partial v}{\partial x} \right)_{u=0} dx = \frac{2\pi nFD c^b r_{\text{tip}}}{\cos v_p} \int_0^{\cos v_p} x \left( \frac{\partial a c r \cos x}{\partial x} \right) dx \\
&= \frac{2\pi nFD c^b r_{\text{tip}}}{\cos v_p} \left( [x a r \cos x]_0^{\cos v_p} - \int_0^{\cos v_p} \arccos x dx \right) \\
&= \frac{2\pi nFD c^b r_{\text{tip}}}{\cos v_p} \left( \sqrt{1 - \cos^2 v_p} - 1 \right) \approx \pi nFD c^b r_{\text{tip}} \cos v_p
\end{aligned} \tag{s14}$$

And get the conclusion

$$I_{ss} \approx \pi nFD c^b r_{\text{tip}} \cos v_p \approx \pi nFD c^b r_{\text{tip}} \sin \theta \tag{s15}$$

where  $I_{ss}$  is the steady-state current,  $n$  is the charge of transferred ion,  $F$  is the Faraday constant,  $D$  is the diffusion coefficient, and  $r$  is the inner pipette radius.

## 1.2 Solid angle model

The second model is the solid angle approach. We can consider the pipette as a solid angle ( $\Omega$ ) in a sphere and the center of which is defined by the tapering of the pipette (Figure S2). It is assumed that the interface at the tip of the pipette is flat and the diffusion field inside the pipette is a part of the spherical diffusion field. Because the steady-state current of spherical diffusion is<sup>[2]</sup>

$$I_{ss} = 4\pi nFD c^b R \tag{s16}$$

We can get the diffusion limiting current of the pipette

$$I'_{ss} = \Omega n F D c^b R \quad (\text{s17})$$

The solid angle is defined as a hole in the sphere of radius R so that

$$\Omega = \pi r_{\text{tip}}^2 / (R^2) = \pi \theta^2 \quad (\text{s18})$$

And the radius of the sphere is simply

$$R = r_{\text{tip}} / \sin \theta \approx r_{\text{tip}} / \theta \quad (\text{s19})$$

So we get the conclusion

$$I'_{ss} = 2\pi n F D c^b r_{\text{tip}} \left( \frac{1 - \cos \theta}{\sin \theta} \right) \approx \pi n F D c^b r_{\text{tip}} \theta \quad (\text{s20})$$

## 2. Calculation results of the effective radii of nanopipettes ( $r < 5$ nm) by equations 3 and 4

To compare the results of  $r$  evaluated by Equations 3 and 4, the transfers of  $\text{TEA}^+$  and  $\text{K}^+$  facilitated by DB18C6 at nano-W/DCE interface were investigated using five pairs of nearly identical nanopipettes (each pair represents two halves of the same pulled capillary and  $r$  of them are supposed to be equal) and calculate  $r$  with Equations 3 and 4, respectively. The data are listed in Table S1. From this table, it is obvious that  $r$  calculated from Equation 3 is  $3.05 \pm 0.36$  times larger than that by Equation 4.

## 3. The transfers of FIT of $\text{K}^+$ by DB18C6 and $\text{ClO}_4^-$ at the nano-W/DCE interfaces

Using the nanopipette voltammetry, we have also investigated the facilitated  $K^+$  transfer by DB18C6 and simple anion transfer of  $ClO_4^-$  using Cell A and C, respectively. In order to obtain high-quality cyclic voltammogram, which is the key for the analysis by three-point method, the background-subtracted has been done to eliminate the effect charging current. Two almost identical nanopipettes, which can be produced by one pulling, have been employed to carry out the cyclic voltammetry with the same potential range and scan rate. One experiment with Cell A (or cell C) without the DB18C6 (or  $ClO_4^-$ ) by one nanopipette is recorded, another experiment with DB18C6 (or  $ClO_4^-$ ) is then carried out. And then, the background-subtracted is done using the software provided by the CHI 910B electrochemical workstation. More importantly, the pulling programs have been modified to pull much shorter taper of the pipette (now is less than 2 mm, it was used to be more than 3 mm). This improvement is important because it can reduce significantly the  $iR$  drop, which mostly comes from the tip of nanopipette, and also can improve the quality of cyclic voltammograms. Silver wire which is used to fabricate reference electrode, has to be reduced from 0.25 mm to 0.15 mm. Fraction with the wall of pipette could block the nano-ITIES! In addition, one needs to take care of shielding, cleanness of the pipette, purity of chemicals. For a steady-state voltammogram at a uniformly accessible electrode, reliable kinetic data can be evaluated only if the following three criteria are satisfied: i)  $|\Delta E_{1/4} = E_{1/2} - E_{1/4}| \geq 30.5$  mV, ii)  $|\Delta E_{3/4} = E_{3/4} - E_{1/2}| \geq 31.0$  mV, and iii)  $|\Delta E_{3/4}| \geq |\Delta E_{1/4}|$ , otherwise the reaction is reversible and no kinetic data can be obtained. Figure S3 is the case for a reversible one, from which no kinetic data can be observed by a 12 nm pipette because  $|\Delta E_{1/4} = E_{1/2} - E_{1/4}| \geq 27.6$  mV, ii)  $|\Delta E_{3/4} = E_{3/4} - E_{1/2}| \geq 27.9$  mV. Figure S4 shows the background-subtracted cyclic voltammograms (Figure S4a for  $ClO_4^-$  and S4b for the FIT process). In these cases, the kinetic data can be extracted based on the method mentioned above, and listed in tables 2 and 3.

#### 4. Estimation of the diffusion layer thickness by equations 3 and 4

The mechanism of simple IT of  $\text{TEA}^+$  is different from that of FIT. In the case of a FIT with excess of aqueous ions inside the pipette, it is a classical TIC/TID mechanism,<sup>1</sup> and the diffusion layer thickness in the organic phase can be obtained from Equation 4

$$I_{\text{ss}} = 3.35\pi nFD_{\text{DB18C6}}cr = \frac{nFD_{\text{DB18C6}}Ac}{\Delta x_{\text{DCE}}} = \frac{nFD_{\text{DB18C6}}\pi r^2c}{\Delta x_{\text{DCE}}} \quad (\text{S21})$$

i.e.

$$\Delta x_{\text{DCE}} = \frac{r}{3.35} \quad (\text{S22})$$

In the case of IT, the diffusion layer thickness in the aqueous phase of the egress reaction of  $\text{TEA}^+$  can be deduced from Equation 3

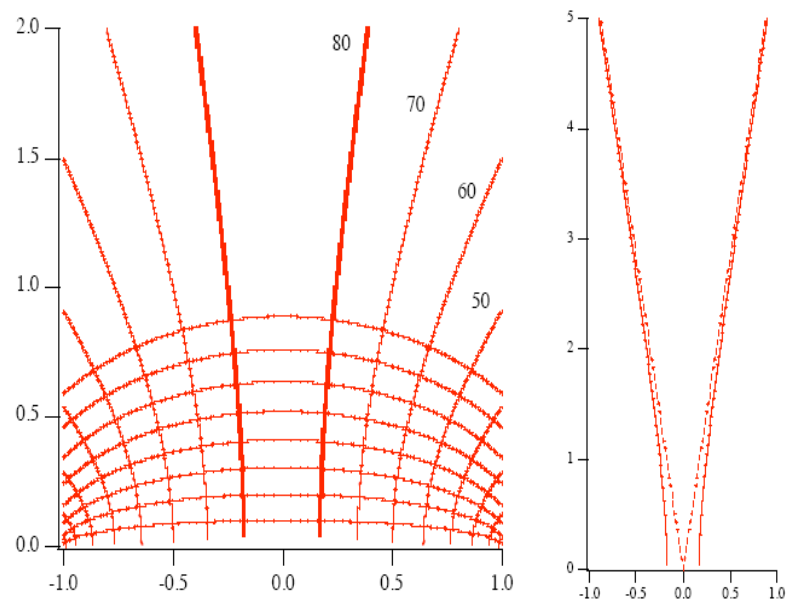
$$I_{\text{ss}} \approx \pi nFD_{\text{TEA}^+}cr\theta = \frac{nFD_{\text{TEA}^+}Ac}{\Delta x_{\text{water}}} = \frac{nFD_{\text{TEA}^+}\pi r^2c}{\Delta x_{\text{water}}} \quad (\text{S23})$$

i.e.

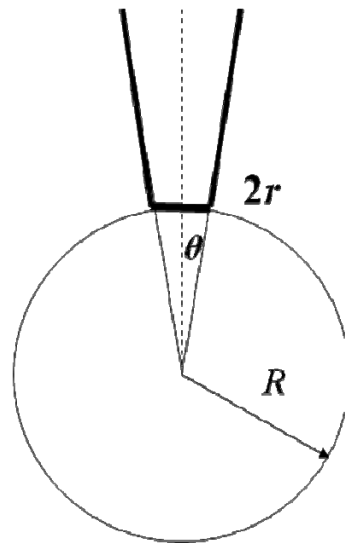
$$\Delta x_{\text{water}} = \frac{r}{\theta} \quad (\text{S24})$$

Thus, the value of  $\Delta x$  is in the range of a few angstrom to a few nanometers. Assuming values of  $\Delta x \approx 1 \text{ nm}$  and  $D_i \approx 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ , one obtains  $k^0 = 100 \text{ cm} \cdot \text{s}^{-1}$  and which is in good agreement with those obtained in this work.

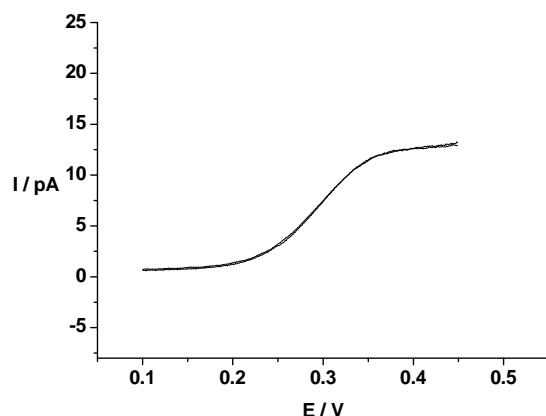




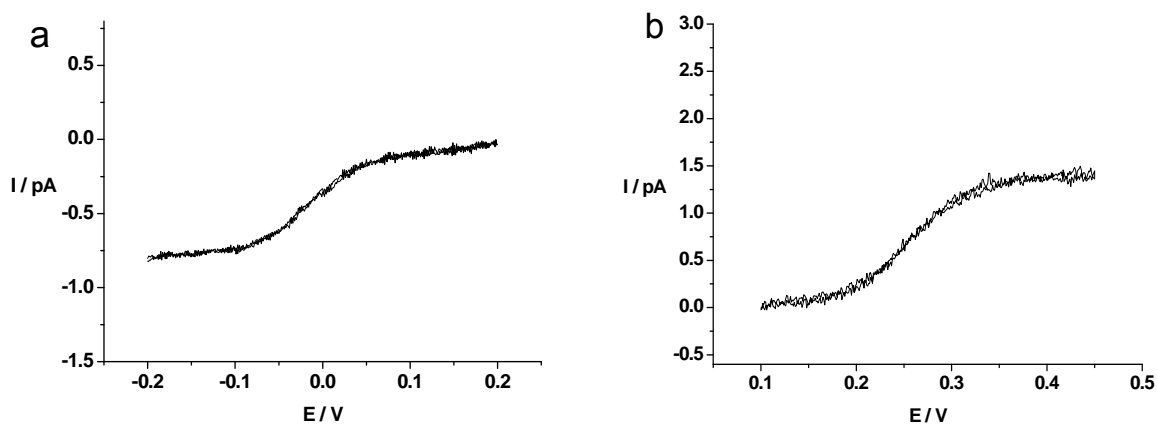
**Figure S1.** Left: Orthogonal ellipse (from bottom to top  $u = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ ) and hyperbola (from the center  $80^\circ, 70^\circ, 60^\circ, 50^\circ, 40^\circ, 30^\circ, 20^\circ, 10^\circ$ ). Right: Pipette for  $v = 80^\circ$ , the dotted line represents  $\tan(v)$ .



**Figure S2.** Scheme of the solid angle model.



**Figure S3.** Background-subtracted cyclic voltammograms of  $\text{K}^+$  transfer facilitated by DB18C6 across the nano-W/DCE interface in nanopipette ( $r \approx 12$  nm) using Cell A. The scan rate =  $50 \text{ mV} \cdot \text{s}^{-1}$



**Figure S4.** Background-subtracted cyclic voltammograms of (a)  $\text{ClO}_4^-$  transfer across the nano-W/DCE interface in nanopipette ( $r \approx 2.4$  nm) using Cell C; (b)  $\text{K}^+$  transfer facilitated by DB18C6 across the nano-W/DCE interface in nanopipette ( $r \approx 1.2$  nm) using Cell A. The scan rate =  $50 \text{ mV} \cdot \text{s}^{-1}$ .

**Table S1.** Comparison of  $r$  evaluated by Equations 3 and 4

Pipette no.	$I_{IT}$ (pA)	$r_{\text{Equation (4)}}$ (nm)	$I_{FIT}$ (pA)	$r_{\text{Equation (5)}}$ (nm)	$r_{\text{Equation (4)}} / r_{\text{Equation (5)}}$
1	0.73	4.78	2.84	1.63	2.93
2	0.37	2.53	1.26	0.72	3.51
3	0.53	3.62	1.89	1.08	3.35
4	1.22	8.33	5.26	3.10	2.69
5	0.34	2.32	1.47	0.84	2.76
mean					3.05±0.36

**References:**

[s1] T. A. Driscoll and L. N. Trefethen, *Schwarz-Christoffel Mapping*. Cambridge, U. K.: Cambridge Univ. Press, **2002**.

[s2] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley: New York, **2001**.